A Low-Cost, Fluorine-Free Electrolyte for Improved Sodium Batteries

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SUMMARY

Sodium batteries are an attractive alternative to lithium-ion technologies due to sodium's lower cost and natural abundance—over 1,000 times greater than lithium, comprising approximately 2.4% of the Earth's crust. However, most current electrolytes rely on fluorine-containing components, which raise economic and environmental concerns. This study explores fluorine-free, borate-based electrolytes that offer improved cycling stability and significant cost and sustainability benefits. We demonstrate stable sodium metal stripping and plating on aluminum foil, enabling anode-free cell configurations with over 50% capacity retention after 700 cycles. Spectroscopic and electrochemical analyses reveal the effects of solvents and salt composition on solvation, ionic conductivity, and oxidative stability. In full-cell configurations, the fluorine-free electrolyte maintains more than 98% capacity retention after 400 cycles. These findings represent a critical step toward the development of cost-effective, environmentally friendly, and high-performance sodium battery systems suitable for future electrification.

KEYWORDS

Energy Storage, Sodium batteries, Anode-free sodium batteries, Fluorine-free electrolytes, Borates

INTRODUCTION

Utilizing cost-effective and more abundant materials in rechargeable batteries offers a sustainable solution for electrifying transportation and increasing the integration of renewable energy in power grids. Sodium batteries (SBs), such as rechargeable sodium-ion batteries (SIBs), have garnered significant attention due to the lower cost and broader geographic accessibility of sodium (Na) and its reserves as compared to lithium (Li) used in the ubiquitous lithium-ion battery (LIB).[1–5] Sodium has nearly a 4x higher mass (22.99u vs. 6.94u) and a higher reduction potential than Li (-3.0 vs. -2.7 V vs. SHE), which results in a lower theoretical energy density for SIBs than LIBs.[6] However, when utilizing a Na metal anode, or anode-free configuration, sodium metal batteries (SMBs) can achieve an energy density comparable to or even surpassing that of LIBs that use a graphite anode and $LiFePO_4$ (LFP) cathode.[7,8] Additionally, anode-free SMBs (AFSMBs) eliminate the need for anode laminates, further reducing battery manufacturing costs. That said, the development of AFSMBs poses a significant challenge, as it requires the Na stripping and plating processes at the negative terminal to be highly reversible. This is extremely challenging when using conventional SB electrolytes, as side reactions due to electrolyte instability irreversibly consume Na^+ ions.[9–12]

Leveraging the successful commercialization of LIBs, the preliminary work in realizing reversible SBs has primarily explored the analogous electrolytes to those used in LIBs, including sodium hexafluorophosphate ($NaPF_6$), sodium bis(fluorosulfonyl)imide (NaFSI), and sodium bis(trifluoromethanesulfonyl)imide (NaTFSI) in carbonate solvent mixtures; however, these initial attempts have failed to fulfill the possibilities of SBs.[13–16] More recently, an intriguing class of anions and related sodium electrolytes based on a tetrahedral boron (B) central atom bound to four alkoxy ligands has been proposed as future SB electrolyte salts.[17–20] This borate framework provides a remarkable template for advanced electrolyte discovery due to the incredible tunability and reasonable synthesis procedure. Additionally, the borate framework provides an opportunity to develop fluorine-free electrolytes, which offer advantages in decreased toxicity, increased ease of recycling, and lower costs.[21] To date, very few fluorine-free SB electrolytes have been reported in literature; but include sodium bisoxaltoborate (NaBOB) and sodium tetraphenylborate (NaBPh). NaBOB-based electrolytes have demonstrated enhanced anti-flammability properties.[22] However, they suffer from inferior cycling performance compared to $NaPF_6$-based electrolytes and lack stability against Na metal, which limits their practical applications.[22] On the other hand, electrolytes containing the NaBPh salt—a commercially available compound currently priced at around \$950/mole from Sigma-Aldrich—demonstrate outstanding stripping and plating capabilities when used with Na metal. However, the limited cathodic stability of this salt has hindered its use as a viable electrolyte option for full-cell applications.[23,24]

Here, we present a fluorine-free sodium tetrakisphenoxyborate salt (chemical formula $NaBO_4C_{24}H_{20}$, abbreviated as NaBOPh) with a scalable synthesis method and an in-depth analysis of its electrochemical properties when utilized in fluorine-free electrolytes. Our synthesis method involves a one-step condensation between two commercially available precursors, which have a combined cost of ~\$43/mole; by contrast, $NaPF_6$ costs ~\$3,600/mole (Sigma-Aldrich). As a result, the NaBOPh salt provides a substantial reduction in cost for SB electrolytes, offering over 98% savings compared to $NaPF_6$. Beyond significant material cost savings, the use of a fluorine-free electrolyte provides additional environmental benefits. Battery recycling processes involving fluorine-containing electrolytes are expensive due to the challenges posed by handling highly corrosive and toxic byproducts, such as HF. Transitioning to fluorine-free systems significantly reduces environmental and cost burdens, making them an attractive alternative.

Our study demonstrates that NaBOPh-based electrolytes facilitate highly reversible Na stripping and plating on an aluminum (Al) foil substrate, even at high current densities. This capability makes NaBOPh-based electrolytes suitable for both SMBs (Na metal anodes) and AFSMBs (limited Na inventory). To gain a deeper understanding of the relationship between the electrolyte's structure and functionality, we conducted both surface and bulk analysis to investigate the ionic solvation structure and chemistry of the electrode-electrolyte interphase. These investigations revealed critical insights into the solubility and oxidation stability of NaBOPh-based electrolytes. The excellent electrochemical cycling performance observed in full-cell configurations, which feature a hard carbon anode and sodium-ion cathodes such as $NaNi_xFe_yMn_zO_2$ (where x+y+z=1, referred to as MNF) or NaFPP (specifically $Na_3Fe_2PO_4P_2O_7$) polyanionic cathodes, clearly demonstrates the potential for using fluorine-free electrolytes for SBs with a variety of cell configurations.

RESULTS AND DISCUSSION

Cost-Effective Synthesis of a Fluorine-Free Electrolyte for Highly Reversible Sodium Stripping and Plating

Fluorine-containing borate salts have been previously synthesized through reactions between metal-borohydride salts and fluorinated alcohols. For instance, borate salt-based electrolytes containing a hexafluoroisopropanol ligand (M^{x+} $[Bhfip]_x^-$) are present in the literature for many monovalent and multivalent batteries, and are produced using metal-borohydride and hexafluoroisopropanol.[25] These synthesis procedures take advantage of the highly reductive nature of borohydride and the acidity of fluorinated alcohols to efficiently form the desired compounds. Inspired by this synthesis concept, we developed the fluorine-free NaBOPh salt through a straightforward condensation reaction between $NaBH_4$ and phenol alcohol as illustrated in **Figure** 1a. The experimental section details our new, efficient method for synthesizing pure NaBOPh, which differs significantly from a previously reported method that utilizes expensive specialty reagents (sodium phenoxide and triphenyl borate).[18] It is likely that previous attempts of using the condensation synthesis were unsuccessful due to the necessity of elevated and prolonged thermal input to overcome the thermodynamic barrier presented by the higher pKa (9.8) of phenol[26], as opposed to 9.3 of hexafluoroisopropanol.[27]

Solution NMR reveals the completion of reaction for NaBOPh as prepared herein, evidenced by a singular peak at 2.54ppm in ^{11}BNMR shown in **Figure** 1b, and lack of borohydride peak (**Figure** S1). As expected NaBOPh shows no resonance in ^{19}FNMR spectra, while $NaPF_6$ displays its characteristic two peaks due to coupling between phosphorus and fluorine. Additionally, we successfully developed a direct electrolyte synthesis that required no final solvent evaporation or salt purification as shown in **Figure** S2. Intriguingly, while NaBhfip has been found to form complexes with DME making removal of synthesis solvent extremely difficult[18], DME can be almost completely removed from NaBOPh salt as shown in the ^{1}HNMR spectrum in **Figure** S3. Further, the NaBOPh salt was shown to be air-stable at 48 hours, as confirmed by no changed in the ^{11}BNMR signal (Figure S4). For complete NMR spectral information see **Figures** S1-S5.

$NaPF_6$ and NaBOPh salts were dissolved in diethylene glycol dimethyl ether (DG) at a concentration of 1M (mol/L) for $NaPF_6$ and 0.4M for NaBOPh to prepare the electrolytes, as detailed in Experimental Section 4.1. Aluminum (Al) foil served as the working electrode and substrate for Na metal stripping and plating, while commercial Na metal chips were used as the counter electrode. Coin cells were assembled using these Al and Na electrodes with both electrolytes. Constant-current Na stripping and plating were conducted at a current density of 0.5mA/cm², with a total deposition capacity of 2mAh/cm² to evaluate the electrochemical and reductive stability of the electrolytes against Na metal, and results are shown in **Figure** 1c. At the beginning of plating, cells exhibit initial ohmic drop, corresponding to Na nucleation on the Al electrode. In the other direction, a flat and stable potential was initially observed for Na stripping from the Al electrode for all cells regardless of electrolyte used. This was followed by a potential spike, indicating that the electrochemical stripping of Na was completed at the Al electrode. The use of 1.0M $NaPF_6$-DG was selected as it showed lower overpotential (**Figure** S6), and higher ionic conductivity (**Table** S6) than 0.4M $NaPF_6$-DG.

Remarkably, the stripping/plating potential of Na remains stable without any increase over 800 hours of cycling for the cells. The Na stripping/plating potentials were approximately 6 mV for the cell with the $NaPF_6$-DG electrolyte and ~18 mV for the cell with the NaBOPh-DG electrolyte. Despite this difference, both electrolytes demonstrated outstanding stability during Na stripping and plating, as confirmed by their exceptionally high Coulombic efficiencies (CEs) throughout the experiment. The NaBOPh-DG electrolyte exhibits slightly less variance (0.609) against a 99.9% efficiency line compared to the $NaPF_6$-DG electrolyte (0.727) over the testing period. This is a critical component for high-performance electrolytes, as the CE discerns Na^+ loss through interphase formation and probes long-term interphase stability which is imperative when using limited Na inventories. These results underscore the ability of both electrolytes to support highly stable and efficient Na stripping and plating processes.

The efficiency of Na stripping and plating at the constant current prompted inquires to understand the electrolyte's performance at elevated current densities. Intriguingly, it was found that NaBOPh supports significantly higher current densities – more than double the critical current density (the maximum current density before a short circuit) of $NaPF_6$ (**Figure** 1d). As is shown, the NaBOPh electrolyte supports current densities up to 8mA/cm^2, while $NaPF_6$ demonstrates short circuiting behavior at current densities greater than 3mA/cm^2. It is also of note that the failure mechanisms of the two electrolytes show marked differences. As opposed to the clear and abrupt short-circuiting behavior seen during cycling for the $NaPF_6$, the NaBOPh electrolyte failure mechanism is more indicative of a soft-short.[28] This means that cells briefly exposed to currents above critical current density for the NaBOPh electrolyte can continue cycling, while the $NaPF_6$ cell failure is irreparable and renders future cell use not only impossible but potentially hazardous as well, as short circuits are a leading cause for fire in battery systems.[29] These results indicate that a fluorinated electrolyte is not necessary for the highly reversible and efficient stripping and plating of Na metal or for utilization in SMBs, and that NaBOPh presents several advantages over traditional fluorine-containing electrolyte salts.

Dendrite-Free Na Metal Deposition with a Fluorine-Free Electrolyte

The highly reversible electrochemical stripping/plating behavior enabled by the fluorine-free NaBOPh electrolyte prompted an investigation of the Na electrochemical deposition with the fluorine-free electrolyte in comparison to that formed from the traditional $NaPF_6$ electrolyte. To this end, a variety of surface and bulk analysis techniques were employed. Firstly, scanning electron microscopy and energy dispersive X-ray spectroscopy (SEM/EDS) were used to visualize the morphology of the electrochemically deposited Na metal. The electrochemically deposited Na metal was collected from cells after Na plating for 2mAh/cm^2 at a current of 0.5mA/cm^2. The disparity of the resulting Na electrodeposition surfaces from the $NaPF_6$ and NaBOPh electrolytes is apparent in **Figures** 2a and 2b. Using the $NaPF_6$ electrolyte (2a), the electrochemically plated Na has a non-homogeneous surface with concentered, fibrous Na depositions. Contrarily, NaBOPh (2b) promotes the growth of uniform, smooth Na metal. Additional SEM images are shown in **Figures** S7-15. The formation of uneven Na plating results in non-uniform, locally-enhanced Na^+ flux, as cations preferentially deposit on surface protrusions, driving the growth of Na dendrites extending into the electrolyte.[30,31] This phenomenon can explain the lower critical current density observed in cells using the $NaPF_6$ electrolyte (**Figure** 1d).

The growth of pre-dendritic Na with a fibrous morphology offers more reactive surface sites for side reactions with electrolytes, leading to continuous consumption of Na^+ ion inventory and ultimately capacity degradation.[32] Fluorine was not significantly detected in the EDS data at the Na surface electrodeposited from the $NaPF_6$-DG electrolyte (**Figure** S11), which is supported by literature that reports the inorganic, NaF-rich region is a thin, inner region of the solid-electrolyte interphase (SEI).[33] NaF's rigidity results in less mechanically robust interphases formed under highly fluorinated electrolyte conditions.[34] Further, a previous report highlights that NaF has significantly higher solubility compared to LiF.[35] This suggests a potential drawback in using fluorinated electrolytes in SBs, as dissolving NaF can lead to an unstable SEI and result in reduced calendar and cycle life.

Electrochemical impedance spectroscopy (EIS) studies were performed for the Na || Al foil coin cells assembling with either $NaPF_6$-DG or NaBOPh-DG electrolytes (**Figures** 2c and 2d). The cell that utilized the $NaPF_6$-DG electrolyte exhibits slightly lower impedance compared to the cell with the NaBOPh-DG electrolyte. The total interfacial resistance was approximately 5 Ω for the NaPF6-DG electrolyte, while it was about 9 Ω for the NaBOPh-DG electrolyte after the first stripping/plating cycle. Additionally, **Figures** 2c and 2d indicate that the interfacial resistance decreases over the course of stripping/plating cycles, suggesting that an interphase with lower resistivity forms, regardless of whether a fluorinated salt is used.

The raw data – shown in **Figures** S16 and S17- were fit to a standard Randles circuit, as illustrated in **Figure** S18. The contribution from charge transfer was not included in the equivalent circuit due to its low values (**Figure** S19). The complete fitting results from the equivalent circuit can be found in **Table**s S1 and S2. The location of the left-most intercept of the semicircle demonstrates that $NaPF_6$ exhibits a lower bulk resistance – or inversely greater bulk ionic conductivity - than NaBOPh. Further the width of the semicircles from the cells with the $NaPF_6$ electrolyte are smaller than those from the NaBOPh-enabled cells. At cycle 20, the resistance values (R_{SEI}) for $NaPF_6$ and NaBOPh are 0.97Ω and 4.97Ω, respectively. By cycle 50 these values have continued to decrease to 0.62Ω ($NaPF_6$) and 3.99Ω (NaBOPh), which demonstrates continued evolution of the SEI during stripping and plating. These differences explain the higher Na stripping/plating overpotential observed in the cell using the NaBOPh electrolyte (shown in **Figures** 1a and 1b) and can be attributed to the low diffusion barrier of Na^+ ions through an F-containing interphase.[36]

The EIS data were later analyzed by Distribution of Relaxation Time (DRT) analysis using an available resource developed in MATrix LABoratory (MATLAB)[37] with the results shown in **Figure** 2e. The faster processes (tau ~ 10^{-5}) demonstrate the resistance of the SEI, while slower processes are a function of the charge transfer resistance and Warburg diffusion.[38] The $NaPF_6$ interphase shows decreased resistance and faster kinetics when compared to NaBOPh; however, both interphases become more conductive with cycling, indicating the formation of a functional SEI with or without fluorine. These improvements can be attributed to the improved multiatom hopping mechanisms of charge carriers through grains within a mature SEI.[39] These results indicate that from strictly a mass transport standpoint, $NaPF_6$ possesses improved capabilities over NaBOPh for both bulk and interphase Na^+ diffusion mechanisms. However, in the case of SMBs and AFSMBs, the smooth and dendritic-free morphology provided by the NaBOPh electrolyte leads to a more uniform Na^+ flux at the surface that is essential for achieving high cycling current densities (**Figure** 1d) and limits electrolyte decomposition by exposure to deposited Na metal for high CE during stripping and plating (**Figure** 1c).

Given these factors, $NaPF_6$ and NaBOPh electrolytes were explored in SMBs that feature a Na metal anode, as well as in AFSMBs assembled using a Na-free, carbon-coated Al foil substrate. Spinel phase lithium titanate ($Li_4Ti_5O_{12}$, LTO) was utilized without any further treatment as the counter electrode in the SMB cells. In the AFSMB cells, a pre-sodiated LTO was employed as the sole source of Na inventory. While the LTO electrode is conventionally considered an anode material in full-cell configurations,[40–42] it was used here as a low-voltage intercalation counter electrode.

Figure 3a shows the highly reversible cycling performance of the NaBOPh electrolyte with an LTO electrode paired with Na metal for over 1000 cycles, demonstrating over 90% capacity retention at the 1000th cycle along with nearly 100% CE throughout the duration of cycling. Notably, a relatively high cycling current density of 134 mA/g (2C) was applied. These results demonstrate the stability of the fluorine-free NaBOPh-based electrolyte in contact with both the Na metal and positive terminal in the cell, as well as compatibility with intercalation-type electrodes.

One major effort in the SB community is the development of chemistries that allow for anode-free cell configurations. This would enable SBs to achieve energy densities higher than 300 Wh/kg.[7,8,43] It has been shown that the use of a highly-porous three-dimensional carbon coating on Al foil offers improved Na deposition and nucleation in AFSMBs due to the dramatic increase in surface area over a conventional Al foil substrate.[44] This effect has similarly been achieved utilizing a nanoparticle enriched substrate surface.[45] Other efforts on the electrolyte front demonstrate the effect of a formate-based additive to the effect of smoothing the morphology of the SEI and deliver improved long-term cycling performance.[46] Further, glyme-based solvents have been reported on multiple accounts to support Na metal deposition and nucleation, and find use in AFSMBs.[47,48]

Here, we introduce an innovative approach to developing AFSMBs by utilizing our fluorine-free NaBOPh electrolyte. To the best of our knowledge, this marks the first successful demonstration of a halogen-free AFSMB, offering safer and more sustainable energy storage solutions. As shown in **Figure** 3b, the NaBOPh electrolyte demonstrates high CE and dramatically improved capacity retention compared to the $NaPF_6$

electrolyte over hundreds of cycles at a rate of 37 mA/g (C/2). By cycle 200, the $NaPF_6$ electrolyte delivers less than 25% of its original charge, whereas the NaBOPh electrolyte maintains 78.6% (85mAh/g) of its original capacity. Further, the NaBOPh-enabled AFSMB remains above 50% of its original capacity beyond cycle 600, whereas the $NaPF_6$-enabled AFSMB demonstrates no appreciable capacity beyond cycle 400. Voltage profiles for these cell builds are shown in **Figures** S20 and S21. The impressive cycling stability offered by the NaBOPh electrolyte can be attributed to its enhanced reductive stability at the anode (Section 2.4) and the smooth Na deposition and nucleation morphology, as discussed. This morphology minimizes the formation of fibrous and pre-dendritic structures within the cell, thereby reducing the amount of "Dead Na" which irreversibly consumes Na inventory and negatively impacts the overall performance.

Anion Effects on Sodium Salt-Solvent Coordination

Compared to the extensive research focused on fluorine-containing electrolytes, there has been relatively little investigation into cation diffusion, solvation structure, and solubility for fluorine-free salts. The strong electronegativity of fluorine enables high solubility and ionic conductivity of fluorinated salts in aprotic solvents; however, this raises the question of whether fluorine-free salts can achieve similar solubilities and conductivities. We conducted solvation structure characterization to address these questions and to understand the differences in bulk Na^+ transport and electrodeposition properties between $NaPF_6$ and NaBOPh-based electrolytes. First, Raman spectroscopy was employed to characterize the local solvent-salt coordination environment for the electrolytes made with $NaPF_6$, NaBOPh, and NaBPh salts. Details regarding solution preparation and characterization conditions can be found in the Experimental section.

The spectra over the ranges of 1120–1160 cm^{-1} and 1400–1500 cm^{-1} were analyzed to compare the solvent-Na^+ interactions between electrolytes, as shown in **Figure** 4a. Between 1400 and 1500 cm^{-1}, the spectrum from the NaBOPh electrolyte closely resembles that of the solvent-only sample. The vibrational modes in this region are assigned to O-C stretching modes of the diglyme solvent molecules.[49] Conversely, the spectra of the $NaPF_6$ and NaBPh electrolytes exhibit reduced Raman activity in this region. Density Functional Theory (DFT) computed Raman spectra shown in **Figure** 4b predicts that these vibrational modes are diminished as a result of solvation-chelation of Na^+ cations dissociated from the salt by DG in the bent configuration, as described elsewhere.[50–52] This mode of Na^+-DG interaction is not exhibited by the NaBOPh electrolyte, resulting in a Raman spectrum with the same intensity near 1500 cm^{-1} as the pure DG solvent. The DG chelation of Na^+ cations was observed in the sodium tetrakishexafluoroisopropyl borate (NaBhfip) electrolyte, which exhibits nearly an identical spectrum to the $NaPF_6$ electrolyte (**Figure** S22). Lower frequency vibrational modes are more challenging to deconvolute due to the energetic overlap of common organic motifs, yet they may suggest aggregate ion-pair-solvent interactions.[53] These findings indicate that NaBOPh does not dissociate as effectively as the other two electrolytes, which is further supported by experimental observation of its limited solubility of 0.4M in DG, compared to over 3M for $NaPF_6$ and 2M for NaBPh in DG at room temperature.

To clarify the origin of the different bulk solvation structures among electrolytes, DFT calculations paired with Bader charge analysis were utilized with results shown in **Figures** S23-25 and **Tables** S3-5.[54] It was observed that BOPh anions distribute electron density differently than the other anions studied, as illustrated by DFT charge densities of relaxed molecular structures, shown in **Figure** 4c. In the case of $NaPF_6$, Bader charge analysis reveals the anion distributes excess electron density over the exterior of its anion shell, which is stabilized by the highly electron-withdrawing fluorine atoms. Similarly, the slightly electronegative anion of the NaBPh salt delocalizes its charge over the carbon atoms of the outer aromatic benzene rings. Conversely, the negative charge of NaBOPh localizes over the inner oxygen atoms between the central boron atom and the phenolic benzene rings. When comparing two equivalent aromatic carbons from NaBOPh (C26, **Figure** S24) and NaBPh (C9, **Figure** S25), the carbon in NaBOPh exhibits a nearly neutral ground state charge of 0.025 electrons, while the analogous carbon in NaBPh has a charge of 0.155. Notably, the higher electronegative oxygen atoms of NaBOPh have an average charge of 1.338 electrons. We hypothesis that the high density of negative charge around the oxygen atoms in NaBOPh more effectively confines the Na^+ cation near the center of the BOPh anion, thereby reducing Na^+-solvent chelation. To quantify the propensity of the salt pair to dissociate, DFT association energies were calculated following **Equation** 1 using methods described elsewhere, which calculate the salt-pair and ion free energies with an explicit DG solvent molecule.[55] The results for NaBOPh, NaBPh, and $NaPF_6$ are depicted in **Figure** 4d, and show that Na^+ ions exhibit the strongest binding energy (more negative value) for the NaBOPh salt. This indicates a more strongly bound Na^+-anion pair in the NaBOPh-DG electrolyte as compared to the $NaPF_6$-DG or NaBPh-DG electrolytes, resulting in less Na^+-DG interactions in the NaBOPh electrolyte.

$$\Delta G_a = G_{pair} - (G_{anion} - G_{cation}) \tag{1}$$

These computational results are further validated through Electro-spray Ionization (ESI) Mass Spectrometry (MS) results as shown in **Figure** 4e. During ESI-MS, charged droplets of solvated ions are electro-sprayed and travel through an aperture, where they are detected using the Time-of-Flight (TOF) technique based on their mass/charge ratio (m/e). Each cationic species corresponds to a solvated Na^+ ion, whose m/e value directly indicates its chemical structure, while the abundance of each species reflects the relative population of each structure in the solvation sheath.[56] In this study, equimolar electrolytes were used directly without dilution to accurately characterize the real solvation environment. To ensure smooth spraying at the nozzle, the chamber was heated to 300°C under a flow of inert gas (Ar). As a result, the ESI-MS only provides information about the partial solvation sheath, which contains only the solvent molecules that are most tightly coordinated with Na^+ ions.[56–58] This offers insight into the desolvation sheath in the SEI-forming layer near the electrodes.

Figures S26-28 display the complete ESI-MS plots of the $NaPF_6$-DG, NaBOPh-DG and NaBPh-DG electrolytes. As DG solvent was the only solvent used in this experiment, the cation mass spectrum of the Na electrolytes include the species $[Na(DG)]^+$, $[Na(DG)_2]^+$, and $[Na(DG)_3]^+$, and indicate that $[Na(DG)]^+$ and $[Na(DG)_2]^+$ are the major components. When comparing the ratio of Na-2DG solvates to Na-1DG solvates, $NaPF_6$-DG and NaBPh-DG electrolytes show ratios of 18.2% and 14.1%, respectively, while NaBOPh-DG has a ratio of only 10.8%. The tighter binding of the cation in NaBOPh sterically restricts the number of DG molecules that can coordinate to the Na^+ ion. Furthermore, due to electronic screening from the anion, there are likely fewer Van der Waals interactions between the dipole moments of the DG solvent molecules and the Na^+ cation for NaBOPh. This, combined with computational modeling, suggests that the absence of fluorine in our salt structure leads to stronger Na^+ - anion pairs, limiting salt dissociation in the DG solvent and resulting in relatively lower ionic conductivities for NaBOPh at equimolar compositions (**Table** S6).

DG is known to be a solvent of moderate to low polarity, with a dipole moment of just 1.92D. To improve the dissociation of the NaBOPh salt, we propose adding a highly polar solvent to our electrolyte solution. Ethylene carbonate (EC), which has a dipole moment of 4.9D, was chosen to create an EC-DG mixed solvent for dissolving the NaBOPh salt. Using a mixed EC-DG solution in a 1:2 v/v ratio enhanced the solubility to approximately 1M, compared to only 0.4M in pure DG solvent (**Table** S6). We believe that the direct interaction between Na^+ and the localized electron density on carbonyl group of the EC molecule can more effectively pull the Na^+ cation away from the BOPh anions. This results in nearly double the ionic conductivity for 1M NaBOPh in the EC:DG mixture (2.89 mS/cm) compared to the standard 0.4M NaBOPh in DG (1.61 mS/cm) (**Table** S6). This strategy was further investigated by adding another high dipole molecule, succinic anhydride (SA, structure shown in **Figure** S29), which has a dipole moment of 4.48D, to the NaBOPh-DG electrolyte. Similar to EC, the solubility of NaBOPh can be enhanced to 0.75M when using a 1M SA in DG solvent solution. This higher concentration NaBOPh-based electrolyte displayed no observable increase in viscosity and was able to wet the separator completely (**Figure** S30).

Oxidation Stability of Electrolytes

The oxidation reactions of electrolytes at the cathode are complex due to the various components present, including solvent molecules and intricate cation and anion solvation clusters.[59] Oxidation reactions at the cathode play a critical role in battery performance because these reactions dictate the composition of the passivation layer formed at the cathode, known as the cathode-electrolyte interphase (CEI).[60] The CEI plays a significant role in determining the reversibility and kinetics of electrochemical reactions at the cathode.[61] Similarly, the reduction reactions of electrolytes at the anode influence the composition of the passivation layer formed at the anode, referred to as the SEI. For new salts and electrolytes, understanding the oxidation and reduction stability is even more critical. This knowledge not only aids in selecting compatible cathodes and anodes that operate within the electrochemical stability window of an electrolyte but also provides insights for optimizing the SEI and CEI passivation layers to enable long-term cycling with minimal capacity loss.

DFT was used to compute the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energies. The HOMO and LUMO computed from DFT at the range-separated hybrid level of theory have been utilized to understand the electronic properties of isolated molecules.[62] The reduction and oxidation potentials of organic substances are correlated with their electron affinities and ionization potentials, as computed by DFT HOMO and LUMO energies, and this correlation is particularly effective for certain isolated organic molecules, such as benzenoid and non-benzenoid hydrocarbons.[63]

As the first step in our systematic investigation of the proposed new salt, we computed the HOMO and LUMO energies for NaBOPh, which are illustrated in **Figure** 5a. The fluorine-free borate salts (NaBOPh and NaBPh) exhibit higher HOMO energies, suggesting that they may be less stable against oxidation compared to the $NaPF_6$ salt. The lower HOMO energy of the $NaPF_6$ salt can be attributed to the electrophilic nature of the fluorine atoms that stabilize the occupied electronic states, evidenced by its HOMO containing significant contributions from the fluorine atoms.[64] Thus, when fluorine atoms replace the hydrogen atoms of the benzene rings of NaBOPh, the fluorinated NaBOPh exhibits a HOMO energy greater than 1 eV lower than that of NaBOPh (**Figure** S31). However, extrapolating the exact oxidation and reduction potentials of electrolytes from the HOMO and LUMO energies of the salts or solvents can be challenging and potentially misleading for the development of electrolytes.[62,65,66] Furthermore, it is important to consider the coupling of redox and chemical reactions occurring at the surface of the electrodes, in addition to the kinetics of these reactions to identify the most relevant processes during electrochemical cycling.[65,66] Additionally, the respective desolvation and pre-desolvation structures of the electrolyte will affect which species are present in the CEI forming region.[60]

To investigate the redox stability of electrolytes and assess their potential for reduction and oxidation at the anode and cathode, respectively, cyclic voltammetry (CV) was employed for cells assembled with an Na metal anode and an Al current collector as the counter electrode. **Figure** 5b shows the CV plots for both $NaPF_6$-DG and NaBOPh-DG electrolytes, measured between 0 and 4V vs. Na/Na^+. During the initial cycle, both electrolytes exhibited oxidation reactions just below 3V; however, these low-voltage oxidation reactions are suppressed in subsequent cycles due to high-voltage interphase formation. At cycle 5, the NaBOPh-DG electrolyte shows an onset of oxidation reactions at approximately 3.4V while the NaPF6-DG electrolyte exhibits negligible oxidative current at this point. In terms of anodic behavior, NaBOPh-DG exhibits significantly improved reductive stability compared to $NaPF_6$-DG, as observed both experimentally and predicted by its higher LUMO energy. Specifically, NaBOPh-DG experiences considerably less reductive current below 1V vs Na/Na^+ than $NaPF_6$-DG during the first CV cycle and continues to display lower reductive current in this voltage region with continued cycling. This stability against reduction contributes to the improved CE observed during stripping and plating, in addition to the morphological arguments discussed in Section 2.1 (**Figure** 1c).

CV measurements of the NaBPh-DG electrolyte against Al current collectors in the voltage range of 0-3.4V vs. Na/Na^+ indicate that oxidation reactions initiate just above 3V vs. Na/Na+ (**Figure** 5c). In this way, the NaBPh-DG electrolyte behaves similarly to the NaBOPh-DG electrolyte, which is consistent with their comparable HOMO energies. However, when the voltage range is expanded to 0-4V vs. Na/Na^+, the

NaBPh-DG electrolyte begins to undergo near catalytic decomposition, as its oxidation products not only fail to passivate against further oxidation but promote electrolyte reactivity throughout the entire voltage range (**Figure** 5d). This observation was further substantiated by chronoamperometry experiments, where cells were held at a constant voltage of 4V vs Na/Na$^+$, as shown in **Figure** 5e. The NaBOPh-DG is seen to effectively passivate the Al foil against electrolyte oxidation during this experiment. The NaBPh-DG electrolyte meanwhile shows an initial decrease in current but subsequently exhibits an increase in cathodic current for the duration of the experiment, suggesting that the NaBPh electrolyte may not tolerate over-charging or voltage spikes (beyond 3.4 V vs. Na/Na+), which are common in commercial-grade battery applications. Furthermore, we hypothesize that the transition metal oxide materials typically used in Na-ion battery cathodes could exacerbate these catalytic side reactions at the surface of cathodes, making this phenomenon even more pronounced in a complete cell configuration.[59] Thus, the NaBOPh salt presents an improvement in cathodic stability over the commercially available fluorine-free sodium salt of NaBPh. Additionally, NaBOPh offers economic benefits, as it can be synthesized for just over \$40/mole, while NaBPh costs ~\$950/mole, according to information from Sigma-Aldrich. Still, enhancing oxidative stability through a better understanding of oxidation mechanisms at the surface of cathodes by using computational methods and characterization studies is a significant motivation for our group moving forward.

Full Cell Testing and Analysis

The effective passivation behavior of the NaBOPh electrolytes was further illustrated in a full-cell SIBs using a $Na_{0.85}Mn_{0.5}Ni_{0.4}Fe_{0.1}O_2$ (MNF) cathode[67] and a hard carbon anode. To the best of our knowledge, this is the first demonstration of a fluorine-free electrolyte (composed of fluorine-free salts and solvents) for an MNF full cell. Complete details regarding electrolyte compositions can be found in Experimental section 4.1. The full cells assembled with $NaPF_6$ and NaBOPh electrolytes were cycled at a rate of 16.5 mA/g (C/3) between 1 and 3.4V to accommodate the oxidation potential limitation of the NaBOPh electrolyte (Section 2.4). While cells of each electrolyte composition experience initial capacity degradation during early cycles, the cells using an NaBOPh electrolyte exhibit significantly better capacity retention than those assembled with an $NaPF_6$ electrolyte (**Figure** 6a). In the early cycles, the CE for the cells using the NaBOPh electrolyte is less than 100%, indicating side reactions of the electrolyte during the formation of the SEI and CEI. However, the cells using the NaBOPh electrolyte quickly stabilize, exhibiting stable capacity retention after ten cycles and a rapid increase in CE. In contrast, while the cells with $NaPF_6$ electrolyte maintain a CE close to 100%, they continue to degrade over the subsequent cycles. At cycle 400, the cells using an $NaPF_6$ electrolyte deliver 87.8% of their initial discharge capacity, compared to 98.0% observed in the cells with an NaBOPh electrolyte. Notably, attempts to use the NaBPh electrolyte for full-cell cycling were unsuccessful, as rapid and extreme capacity degradation occurred in these cells (**Figure** S32). Therefore, the NaBOPh electrolyte effectively passivates the MNF cathode, despite both NaBOPh and NaBPh exhibiting similar HOMO energies and oxidation potentials (Section 2.4) of approximately 3.4V vs. Na/Na$^+$.

The cells were also cycled at various rates to evaluate the impact of the fluorir 4V hold on rate performance, as shown in **Figures** S33 and S34. The cells assembled with $NaPF_6$ or NaBOPh electrolytes demonstrate a reversible capacity of approximately 72 mAh/g and 70 mAh/g between 1 and 3.4V at a cycling rate of 7.4 mA/g (C/10). At higher cycling rates, the $NaPF_6$ electrolyte shows improved rate performance, as the NaBOPh electrolyte cell capacity decreases at rates faster than 37mA/g (C/2). This finding contrasts with the NaBOPh electrolyte's capability for rapid Na metal stripping and plating (up to 8 mA/cm², Section 2.1 and 2.2) in SMBs. We believe this discrepancy arises from the greater pre-desolvation barriers imposed during Na$^+$ insertion into hard carbon for the NaBOPh electrolyte due to the greater anion influence in its solvation structure when compared to the $NaPF_6$ electrolyte.[68]

The voltage profiles of the 1st cycle and the 200th cycle are compared in **Figure** 6b. It is evident that both $NaPF_6$ and NaBOPh electrolytes allow for reversible cycling in the MNF/HC cells, with both electrolyte chemistries demonstrating over 90% capacity retention after 200 cycles That said, a higher charging potential is observed in the NaBOPh cells. This may be attributed to the reduced bulk cation transport capability of the NaBOPh electrolyte and lower ionic conductivity of the resulting interphases. However, superior capacity retention is observed for the NaBOPh electrolyte as compared to $NaPF_6$ indicating more effective passivation of SEI and CEI.

The differential capacity curves (dQ/dV) at the 100th cycle, shown in **Figure** 6c, reveal one pair of peaks for Na^+ intercalation/deintercalation for the MNF cathode with the NaBOPh electrolyte. In contrast, two peaks were observed in the dQ/dV for the cells using $NaPF_6$. The appearance of the second pair of peaks at higher voltage can be attributed to the lower charge overpotential for the $NaPF_6$ electrolyte. Moreover, the charge-discharge hysteresis is greater for the cells using NaBOPh compared to those with $NaPF_6$. **Figures** S35 and S36 exhibit the dQ/dV plots from the 1st and 200th cycles for the cells with $NaPF_6$ and NaBOPh electrolytes, respectively. In the dQ/dV plots for the cells using $NaPF_6$, the peaks remain at relatively constant positions, but their relative amplitudes decrease in the aged cell, indicating capacity degradation. A slight increase in hysteresis is observed for the cells with NaBOPh; however, the amplitude of the peaks remains consistent, signifying less capacity degradation.

Following the promising cycling performance observed in the coin cells evident in **Figure** 6a, the NaBOPh electrolyte was further tested in a pouch cell configuration. To better accommodate the upper voltage limitation of NaBOPh, we purchased dry pouch cells from Li-FUN Technology Corporation Limited assembled with an NFP cathode and hard carbon anode with a capacity of ~150 mAh. The pouch cells were filled with NaBOPh electrolyte and cycled between 1.5 V and 3.25 V at a cycling rate of 9 mA. **Figure** 6d shows the reversible cycling using the fluorine-free NaBOPh electrolyte in the pouch cell format. In addition to cycling performance, we observed significant differences in gas generation in the cells with $NaPF_6$ and NaBOPh. The cells with $NaPF_6$ resulted in approximately a threefold increase in cell volume after just 100 cycles (**Figure** S37), while no appreciable gassing was observed in cells with the NaBOPh electrolyte (**Figure** S38). This phenomenon may be attributed to the formation of HF gas due to the decomposition of the PF_6 anion.[69] Furthermore, the decomposition of PF_6 through the generation of HF leads to the formation of PF_5, a Lewis acid that promotes transition metal dissolution from the cathode and subsequent capacity decay.[70]

To analyze the impact of the electrolytes on the composition of the SEIs, X-ray photoelectron spectroscopy (XPS) was conducted on hard carbon anodes harvested from cycled cells after full discharge. The results in **Figure** 6e provide key insights into interphase formation from the two electrolytes. First, the absence of a fluorine signal was confirmed in the XPS analysis of the NaBOPh-enabled interphase. Interestingly, the F 1s region for $NaPF_6$ does not show the presence of NaF. Instead, it displays C-F type bonds, which consist of adsorbed F and semi-ionically bonded F to the hard carbon, at binding energies of 684.4eV and 687.4eV, respectively. Accordingly, the C-F type bonds are shown in the C1s spectra at ~289.2eV. The lack of NaF in a desodiated HC anode, along with the observed C-F bonding modes, has been previously reported in the literature.[71,72] Second, a higher intensity signal for Na_2O was observed in the HC anode using NaBOPh compared to that using $NaPF_6$. This difference is evident in both the Na 1s and O 1s spectra, with the NaBOPh sample displaying a Na_2O area value of 232, while the $NaPF_6$ sample shows a value of 136 in the O 1s spectra. Complete peak parameters can be found in **Table** S7.

Boron-oxygen containing species were also observed in the B 1s region of the surface when using NaBOPh. The solvation structure impacts the chemical composition of the SEI by governing the species available for reduction at the anode surface.[73] As such, it is understandable that central anion fragments of the NaBOPh are involved in the SEI formation, in contrast to $NaPF_6$, where the exterior fluorine atoms participate more significantly than phosphorous in SEI formation. This explains the absence of a phosphorous signal for the $NaPF_6$ samples. The presence of boron species in the SEI has also been reported in other boron-containing electrolytes, such as NaBOB[74,75] and NaBhfip.[76] Additionally, recent research on calcium batteries revealed that a boron-rich SEI leads to a cross-linked, polymeric SEI, which results in uniform calcium electrodeposition, similar to the findings in this study.[77]

CONCLUSIONS AND PERSPECTIVE

Here we present a scalable synthesis method for a fluorine-free salt in NaBOPh that can be used to create fluorine-free electrolytes at a significantly lower economic and environmental cost when compared to conventional fluorine-containing electrolytes. This work demonstrates that a fluorine-free SEI and CEI effectively passivate the surface of anode and cathode, suggesting that fluorine may not be an essential electrolyte component for SBs. Furthermore, these fluorine-free interphases lead to improved cycling performance in multiple cell configurations including SIBs, SMBs, AFSMBs. We attribute this to the unique molecular structure of NaBOPh which results in greater Na^+- interior anion coordination and weaker solvent involvement in the solvation structure which leads to an anion-rich interphase chemistry which was observed in a borate-rich SEI. Also, these effects promote a smoother, more uniform Na electrodeposition surface. Our investigation into Na^+ solvation in fluorine-free electrolytes highlights a significantly different solvation mechanism in the Na^+-BOPh-solvent environment, as compared to $NaPF_6$ electrolytes. Future research should leverage advanced operando surface characterization techniques coupled with computational methods to better understand the solvation/desolvation processes of borate-based electrolytes and their impact on the interphase chemistry. While the absence of fluorine is associated with higher HOMO energies as compared to the lower HOMO energy of the fluorinated NaBOPh, this does not directly imply lower oxidation stability, as the NaBOPh electrolyte presented here demonstrates oxidation stability up to approximately 3.4 V vs Na/Na+, which is comparable to that of the fluorinated NaBOPh[18], and still allows for cathode full cell stability.

In summary, this work opens the door to next-generation electrolyte discovery by introducing rationally designed halogen-free electrolytes that capitalize on the advantages of removing fluorine-containing species from the electrolyte mixture. We expect that NaBOPh-based electrolytes can effectively facilitate high-capacity sulfur-based conversion cathodes including iron sulfide (FeS_2), as well as moderate-voltage cathodes such as chromium-based cathodes and polyanion cathodes.[78–81] However, further advancements in fluorine-free electrolytes and their wide-spread application will rely on enhancing the oxidation stability of the electrolytes, through salt, solvent, additive, and interphase engineering to accommodate higher voltage cathodes. With incredible financial and environmental benefits offered by fluorine-free electrolytes over the conventional electrolytes, our research represents a crucial step toward developing SBs that enable broader adoption in large-scale energy storage systems.

METHODS

Material Preparation:

Sodium tetrakisphenoxyborate (NaBOPh) salt was synthesized utilizing a simple condensation reaction between 1 equivalent of $NaBH_4$ (99.99%, Oakwood Chemical) and 4 equivalents of respective phenol (99.5%, Sigma-Aldrich) in 1.5 equivalents of dimethoxyethane (DME) (99.5% anhydrous, Sigma-Aldrich) that had previously been dried over 4A sieves after 400C exposure for 24hr. NaBhfip was synthesized from 1,1,1,3,3,3 -hexafluoro-2-proponal (99%, Oakwood Chemical). Phenol solid crystals were first dissolved in a DME to form a liquid reagent solution. The alcohol-solvent mixture was added dropwise to $NaBH_4$ in DME a rate of 20 drops per minute at room temperature. After alcohol addition, the reaction was held at room temperature for 1hr as the exothermic evolution of H_2 gas was observed. Following this, the reaction was heated at 80C for 12h. The Reaction mixture was then dried under vacuum at -0.8bar and 85C for 36h and the product was isolated as a white solid. The identity of NaBOPh salt was confirmed using liquid ^{11}BNMR, ^{1}HNMR, ^{13}CNMR and ^{19}FNMR performed on a Bruker 300MHz Instrument in deuterated acetonitrile (99.9%, ThermoFischer). An alternative synthesis route described as a “neat” synthetic procedure was performed utilizing the same reagents, but with the addition of phenol to $NaBH_4$ in diglyme at the desired electrolyte concentrated. The addition rate was 20 drops per min at room temperature, and the reaction was held at room temperature for 1hr. Following this, the reaction was heated at 100C for 18hrs. The ^{11}BNMR of this product can be found in **Figure** S2.

Electrolytes were prepared by dissolving sodium salts in diethylene glycol dimethyl ether (DG) (99%, Sigma-Aldrich), ethylene carbonate (EC) (99%, Sigma-Aldrich), or diethyl carbonate (DEC) (99%, Sigma-Aldrich). Prior to use, solvents were dried over 4Å molecular sieves that had been previously heated at

400C for 24h. Salt were dissolved at room temperature with vortex mixing at their respective concentrations. $NaPF_6$ (99.9%, MSE) and NaBPh (99%, Sigma-Aldrich) were used as received without any further purification. Electrolytes shown in **Figures** 1-5 were formulated in DG solvent at 0.4M for NaBOPh, and 1M for $NaPF_6$. The fluorine-free electrolyte presented in **Figures** 6a-d consists of 1.0M NaBOPh dissolved in EC:DG (1:2 v/v) with 5wt% SA to reach high conductivity and ionic conductivity (detailed in Section 2.3). $NaPF_6$ reference for these **Figures** 6a-e are 1.0M $NaPF_6$ dissolved in EC:DEC (1:2 v/v). XPS data presented in **Figure** 6e for NaBOPh was collected using 0.4M NaBOPh in EC:DEC (1:2 v/v). All above steps were performed in an argon-filled glovebox with less than 1ppm O_2 and 0.1ppm H_2O.

$Na_{0.85}Mn_{0.5}Ni_{0.4}Fe_{0.1}O_2$ (MNF) was synthesized by a solid-state method according to our previous work.[82] Stoichiometric quantities of sodium carbonate monohydrate ($Na_2CO_3 \cdot H_2O$), Nickel (II) oxide (NiO), Manganese (III) oxide (Mn_2O_3), and Iron (III) oxide (Fe_2O_3) were mixed using a planetary ball mill for 4 hours at 500 RPM. The solid-state synthesis used a two-step heating process with heating and cooling rates of 5°C/min. The mixture was heated to 550°C for 5 h and then at 900°C for 14 h followed by cooling to room temperature. The final product was transferred to glovebox (H_2O & $O_2 \leq 0.1$ ppm) and ground thoroughly using agate mortar & pestle to obtain a fine powder. Hard carbon (Kuranode Type 2) was obtained from Kureha Battery Materials Japan Co. Ltd and used without modification.

The $Na_{0.85}Mn_{0.5}Ni_{0.4}Fe_{0.1}O_2$ electrode was prepared by using a Thinky (SR-500) to mix the synthesized powder, conductive carbon (Super P) and polyvinylidene fluoride binder (PVDF) in a mass ratio of 85:7:8 with N-methyl pyrrolidone (>99.5%) as the solvent. Mixing was done in the dry room at the advanced battery facility (ABF) at PNNL, then casted on Al foil (15 μm in thickness) using compact tape casting coater (MSK-AFA-III). After casting the electrodes were dried at 90˚C under vacuum. The hard carbon electrode was prepared by using a Thinky (SR-500) to mix the hard carbon powder (Kuranode Type 2), conductive carbon (SuperP), carboxymethyl cellulose (CMC), and Styrene-butadiene rubber (SBR) in a mass ratio of 93:3:2:2 with H_2O as the solvent. Mixing was done in ambient conditions, then casted on Al foil (15 μm in thickness) using compact tape casting coater (MSK-AFA-III). Electrodes were then dried at 100˚C under vacuum. The LTO electrodes were prepared using spinel phase lithium titanate ($Li_4Ti_5O_{12}$, LTO) purchased from MTI. A FlackTek DAC 330-100 Pro SpeedMixer was used to mix the LTO active material, conductive carbon (C45), and polyvinylidene fluoride binder (PVDF) in a mass ratio of 8:1:1 using N-methyl pyrrolidone (>99.5%) as the solvent. Mixing was done in ambient conditions, then casted on Al foil using a TQC sheen AB3652 compact film applicator. Casted electrodes were then dried at 90˚C under vacuum. Sodiated LTO was formed by constructing cells of Na || LTO configuration with the same electrolyte as intended use later and then performing constant current discharging to 0.1V at $1mA/cm^2$. The cells were disassembled and sodiated LTO electrodes were harvested for use in anode-free cells when paired with Al foil.

Electrochemical Analysis:

Electrochemical measurements were performed in 2032-type coin cells assembled in an argon-filled glovebox with 60ul of electrolyte and a 2325 Celgard trilayer (PP/PE/PP) separator. Unless otherwise noted, cells were tested immediately following their fabrication. Cyclic Voltammetry (CV) experiments were performed on a Biologic VMP-3 instrument and utilized an Na metal counter electrode and aluminum foil working electrode. The battery grade aluminum was used as received. For data presented in **Figures** 5b-d a scan rate of 5mV/s was employed. The data in **Figures** 5e was collected at 4V vs Na/Na^+. Sodium stripping/plating CE measurements as shown in **Figures** 1c and 1d were performed on a Neware Battery Tester and utilized a sodium metal cathode with aluminum foil as the anode. 2mAh cm^{-2} of Na was plated and stripped at a rate of 0.5mA cm^{-2} in each cycle. Electrochemical Impedance Spectroscopy (EIS) experiments shown in **Figures 2**c-e were performed on a Biologic VMP-3 instrument. Surface resistance experiments were performed in Na || Al Foil (1.5cm diameter) cells with a frequency window of 500KHz to 100mHz and a perturbation amplitude of 10mV. Cells were rested 24h prior to experiment. R_{SEI} was found from the width of the resulting semi-circle from the Nyquist plot and fit using the Biologic software. Aging cycling during this procedure was obtained through 0.5h cycles at 0.25mA cm^{-2}. Conductivity measurements were obtained using a Metler Toledo SD23 and InLab 752-6 mm probe. Galvanostatic cycling as shown in **Figures** 3a,b and **Figures** 6a-d was conducted on a Neware Battery Cycler at ambient room temperature (20-23˚C). The cells were rested 24h following fabrication then underwent three 0.1C and two 0.2C cycles as a formation procedure before further testing. Pouch cells as shown in **Figure** 6d were filled with 120uL of electrolyte and cycled under uniform and constant pressure at ambient room temperature.

SEM/EDS Analysis:

After cells were disassembled in an argon-atmosphere glovebox, aged electrodes were transferred to the SEM chamber without air exposure by using portable air-lock chamber. The images of the electrodes were observed by SEM (JEOL JSM-6610LV) equipped with EDS (Oxford Instruments) operating at 20 kV.

Raman Analysis:

Raman data were acquired from areas of interest using a Horiba LabRAM HR Evolution Raman

spectrometer equipped with a 532nm, 100mW frequency-doubled Nd:YAG laser excitation source, 600mm^{-1} diffraction grating, 256x1024 pixel CCD detector, and 50x long working distance (LWD) microscope objective (N.A. 0.5). A laser power of 100% was applied to a spot located just below the surface of a 10µL of electrolyte solution for 10 second acquisitions with three spectra accumulations each. Spectra were collected from 50 cm^{-1} to 1800 cm^{-1} by integrating the counts in the undiffracted, 256-pixel direction of the detector, such that each spectrum contains 1024 points. Resulting spectra were corrected using a 16th order polynomial baseline using LabSpec 6 software (Horiba Scientific, Inc.). The spectrometer was calibrated using the 520 cm^{-1} Raman peak of a reference silica (Si) chip prior to analysis. All electrolyte solutions were prepared equimolar at 0.4M in DG.

Computational Methods:

All molecule structures were first relaxed using the r2SCAN-3C functional. We chose to use the bent configuration of diglyme following the results from ab-initio molecular dynamics calculations.[83] All calculations included the conductor-like polarizable continuum implicit solvation model (C-PCM)[84] using experimentally known values for the dielectric constant and refractive index of diglyme of 7.23 and 1.4097 respectively. The ωB97X-D4 functional with the def2-TZVP basis set was used for HOMO/LUMO and Raman spectra calculations. HOMO/LUMO calculations of salt pairs included one explicit diglyme molecule to complex the Na^+ atom. Raman calculations were found to be insensitive to adding additional diglyme molecules beyond one **Figure** S25. All dissociation energy calculations followed methods previously established for lithium salt association energy calculations.[55] The base aiida-orca code base was forked and edited to correct for ORCA parsing issues on CU Boulder's cluster.

All molecular DFT calculations were performed with the ORCA 5.0.4 package.[85] Multi-step workflows were built and executed using AiiDA.[86] All DFT data presented in this work including starting structures and calculation settings were automatically stored in a PostgreSQL database that was exported from AiiDA and uploaded to: 10.6084/m9.figshare.27164487.

ESI-MS Analysis:

Outside the glove box, 5-µL of the electrolyte solutions were injected directly into the nebulizer of a quadrupole, electrospray-ionization mass spectrometer (Agilent Technologies 6120). Equimolar electrolytes concentrations of 0.4M in DG were used for measurement. The temperature of the argon gas flowing through the nebulizer was set to 300°C. The fragmenting voltage was set to 70 V, and data were collected in the m/e range of 50-1200 Da. The mass spectrometer collected data on the positive and negative ions present simultaneously as full gaussians. The nebulizer was thoroughly cleaned by anhydrous dimethyl carbonate (>99%, Sigma-Aldrich) and high-performance liquid chromatography grade water (Sigma-Aldrich) after each injection.

XPS Analysis:

XPS was performed by using a PHI 5000 VersaProbe II System (Physical Electronics) with a base pressure of 2×10^{-9} Torr. The electrodes were harvested from aged cells of HC | MNF configuration from 0.4M NaBOPh and 1M $NaPF_6$ in EC:DEC (1:2 v/v) and carefully washed with EC:DEC (1:2 v/v) before measurement. The photoelectron spectra were obtained in the fixed analyzer transmission mode using an Al Kα radiation (hv = 1486.6 eV, 100μm beam, 25W) with Ar^+ and electron beam sample neutralization. XPS spectra were aligned to the graphitic carbon at 284.5 eV.

RESOURCE AVAILABILITY

Lead Contact

Further information and requests for resources and reagents should be directed to and will be fulfilled by the lead contact, Chunmei Ban (chunmei.ban@colorado.edu).

Materials Availability

All unique reagents generated in this study are available upon reasonable request.

Data and Code Availability

The datasets supporting the findings of the study are available in the paper and its supplementary information. The altered aiida-orca package and the workflows used in this manuscript can be found at

https://figshare.com/articles/dataset/Final_Publication_AiiDA_Archive/28047047/1?file=52392398 with code accessible at https://zenodo.org/records/15579754.

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AUTHOR CONTRIBUTIONS

E.S.F., N.R.S., and C.B. initiated and designed the research. E.S.F. and N.R.S. conducted experiments related to the synthesis, morphology, structure, and electrochemical properties. N.R.S. and C.T. performed computational simulation experiments. M.L. and X.L. provided the NMF and HC electrodes used in the electrochemical characterization. S.S. conducted the air-free XPS and ESI-MS experiments. C.B. coordinated and supervised the research, while C.M. supervised the computational experiments. E.S.F. and C.B. drafted the manuscript, with the entire team contributing to its editing.

DECLARATIONS OF INTEREST

E.S.F., N.R.S., and C.B. are the inventors of a related international patent application. University of Colorado Boulder owns intellectual property on the electrolytes disclosed here. The intellectual property is currently licensed.

SUPPLEMENTAL INFORMATION

Supplemental information can be found online at

FIGURE TITLES AND LEGENDS

Figure 1: Synthesis scheme and sodium stripping/plating analysis. a) Synthesis route of NaBOPh described herein. b) ^{11}BNMR and ^{19}FNMR of NaBOPh and $NaPF_6$. Purple represents NaBOPh (^{11}B NMR (96 MHz, CD_3CN) δ 2.54.) and green is $NaPF_6$ (*^{19}F NMR (282 MHz, CD_3CN) δ -71.61, -74.12).* c) Voltage profile of Na stripping and plating with the SMB coin cell (Na || Al foil) configuration, at a current density of 0.5mA/cm^2 for 2mAh/cm^2 per cycle. Dots represent CE (scale at right), traces represent voltage vs Na/Na$^+$ (scale at left). d) Elevated current density testing results in coin-type SMBs of Na || Al foil configuration. Current density is plotted as grey dashed trace and scaled at right. Red outlines show time of cell failure: 3.25mA/cm^2 for $NaPF_6$ (green), 8mA/cm^2 for NaBOPh (purple).

Figure 2 – Effects of electrolytes on na electrodeposition. a) SEM/EDS of $NaPF_6$ Na deposition on Al foil in coin cell. b) SEM/EDS of NaBOPh Na deposition on Al foil in coin cell. c) Fitted EIS of $NaPF_6$ in Na || Al foil coin cell. d) Fitted EIS of NaBOPh in Na | Al foil coin cell. e) DRT analysis of $NaPF_6$ (green) and NaBOPh (purple). Inset of representative cell configuration and SEI structure.

Figure 3 – SMB (a) and AFSMB (b) cycling results. a) SMB coin cell cycling data with NaBOPh electrolyte of Na | LTO configuration. Purple solid markers represent cell specific capacity, purple open markers are CE (%). b) AFSMB coin cell cycling data of Na-LTO | C-Al foil configuration. Solid markers represent capacity retention (%) (left scale), and open markers are CE (%) (right scale). Purple markers are NaBOPh, green markers are $NaPF_6$. A gold region of 99.0-100% CE is highlighted.

Figure 4 – Solvation structure and anion electronic configuration analysis. a) Raman spectroscopy of equimolar sodium salts in DG: NaBOPh in purple, $NaPF_6$ in green, NaBPh in orange, DG in black. b) Simulated Raman with DG-Na$^+$ chelation complex (blue) and pure DG (red). Traces are the result of moving summation of discrete wavelength results. c) DFT charge densities rendered in VESTA of sodium salts. Atomic colors: Oxygen (red), Boron (green), Carbon (brown), Hydrogen (white), Phosphorous (purple), Fluorine (blue). Electron density isosurfaces are shown on top of the molecular structures where blue indicates regions of greater electron density than yellow. d) Na$^+$ binding energy tabulation of sodium salts. e) Positive ion mass spectroscopy data of sodium electrolytes. Ratio of 2DG / 1DG per Na$^+$, where higher value indicates more Na$^+$-2DG interactions.

Figure 5 – Studies of the electrochemical stability of electrolytes. a) HOMO/LUMO energies for sodium salts. Molecular orbitals are plotted where blue represents negative phase and red is positive phase. Atom colors: P (orange), F (blue), B (pink), C (dark grey), H (light grey), O (red), Na (purple). b) CV of NaBOPh (purple) and $NaPF_6$ (green) electrolytes in coin cell with Na | Al foil configuration 0-4V window. Cycle 1 is the light trace, cycle 5 is the darker color. c) CV of NaBPh cycle 1 (light orange) and cycle 5 (dark orange) in 0-3.4V window. d) CV of NaBOPh (purple) and NaBPh (orange) 0-4V vs Na/Na$^+$ cycles 1 (light) and 5 (dark). e) Chronoamperometry of sodium electrolytes at 4V vs Na/Na$^+$ in coin cells of Na | Al foil. NaBOPh is shown in purple, and NaBPh in orange.

Figure 6 – Fluorine-free electrolytes enabled full cell cycling. a) Capacity retention plot for sodium electrolytes of NaBOPh (purple) and $NaPF_6$ (green) in coin cells of MNF || HC configuration. Solid markers are capacity retention, hollow are CE. Golden area represents CE of 99.0-100%. Cycling parameters of 1.0-3.4V at C/3 (16.5 mA/g). b) Relative capacity voltage profiles of cells from (a). Light traces cycle 1, darker traces cycle 200. c) dQ/dV plot of cell data from (a) at cycle 100. d) Capacity retention plot of NaBOPh electrolyte cycling in pouch cells of NFP || HC configuration. 1.5-3.25V window at C/20 rate (9mA). e) XPS of HC electrodes prepared from sodium electrolytes cycled in coin cells of MNF || HC configuration. NaBOPh sample is top purple trace in all subfigures, $NaPF_6$ is bottom green. Peak assignments are listed in their respective color as labeled.

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